

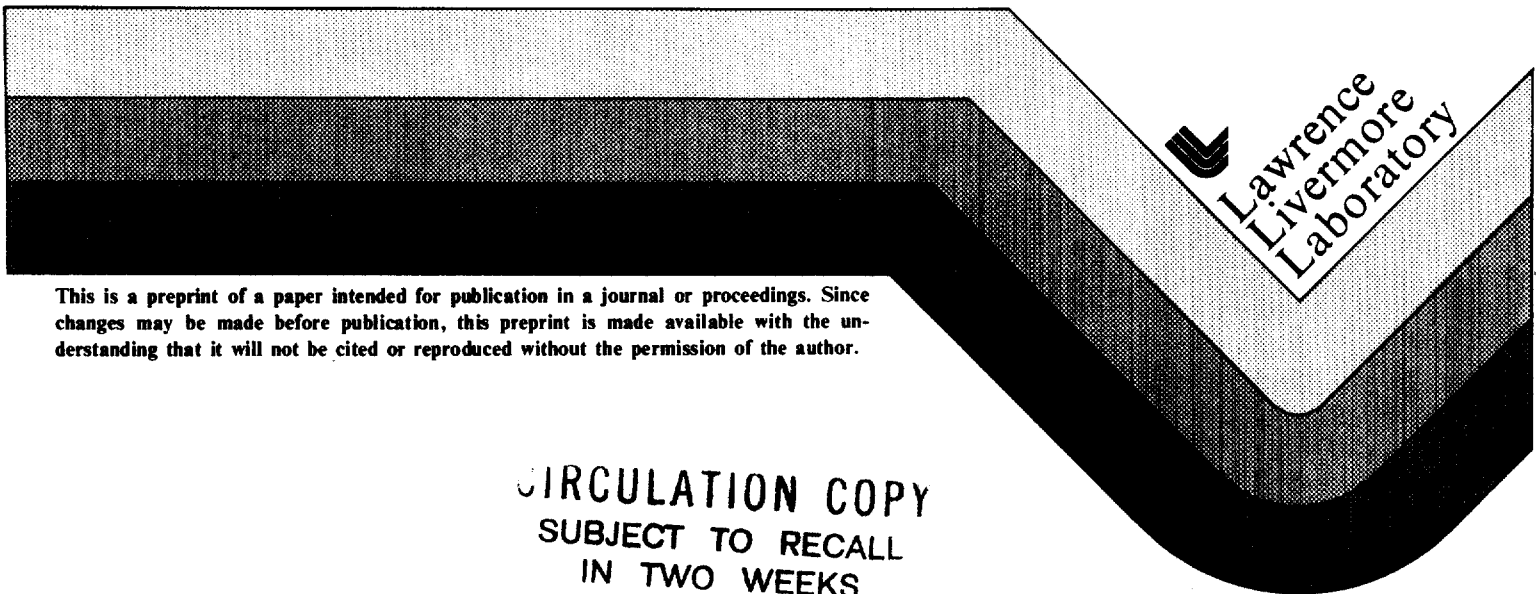
UCRL- 84763
PREPRINT

METAL ORGANIC - CHEMICAL VAPOR DEPOSITION
FABRICATION OF SEMICONDUCTOR LASERS

Christopher Thomas

NTA - 52nd Annual Convention, Chicago Illinois
August 12 - 16, 1980

August 6, 1980



This is a preprint of a paper intended for publication in a journal or proceedings. Since changes may be made before publication, this preprint is made available with the understanding that it will not be cited or reproduced without the permission of the author.

DISCLAIMER

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

METAL ORGANIC - CHEMICAL VAPOR DEPOSITION FABRICATION OF SEMICONDUCTOR LASERS*

Christopher Thomas**

Abstract

The Metal Organic-Chemical Vapor Deposition (MO-CVD) process will be studied and implemented in detail. Single crystal GaAs, and $\text{Ga}_x\text{Al}_{1-x}\text{As}$ films will be grown on GaAs by depositing metal-organic alkyl-gallium compounds in the presence of an arsine mixture. The metal-organic chemical vapor deposition process will allow formation of the semiconductor compound directly on the heated substrate in only one hot temperature zone.

With MO-CVD, semiconductor films can be efficiently produced by a new more economical, less complicated process which will lend itself more easily than past fabrication procedures, to high quantity, high quality reproduction techniques of semiconductor lasers. Clearly MO-CVD will be of great interest to the communication industry where semiconductor lasers will be used extensively in fiber optic communication systems, and similarly to the solar energy business where GaAs substrates are used as photoelectric cells.

Introduction

The Metal Organic-Chemical Vapor Deposition (MO-CVD) process will be studied and an engineering model thereof described. MO-CVD is a vapor phase epitaxial growth process whereby thin film semiconductor lasers are produced by reacting a vapor flow of metal organics and hydrides on a substrate. In the research discussed here, the films produced are GaAs, and $\text{Ga}_x\text{Al}_{1-x}\text{As}$ of various p and n dopant levels and in general grown on GaAs insulating substrates. These film compositions are chosen because of their potential

*Work partially performed at the University of Texas Engineering Department and under the auspices of the U.S. Department of Energy under contract W-7405-ENG-48, by the Lawrence Livermore National Laboratory.

**Student at University of Texas and summer employee at Lawrence Livermore National Laboratory - 1980

application in military and commercial devices. Their respective emission wavelengths are the most attractive characteristics with GaAs emitting in the infrared region and $\text{Ga}_x\text{Al}_{1-x}\text{As}$ emitting over a region of the visible spectrum.

Vapor phase epitaxy (VPE) growth processes have several advantages in common. Single crystals and epitaxial layers of high purity and crystalline perfection are attainable, as well as accurately controllable thickness and doping profiles. MO-CVD is one of several scientifically feasible fabrication techniques of the VPE family. Among the advantages of MO-CVD over some other VPE processes is that it should be easily extendable to commercial production demands of high volume and simple process control.

Most processes developed previous to MO-CVD involve at least a two-temperature zone in the reactor region which must be accurately controlled. Most multi-temperature epitaxial growth processes typically require a transporting agent and etching specie thus making doping a complicated process. MO-CVD requires a single temperature zone with no etching specie needed. Experimentally it has been shown that film quality is not affected greatly by temperature variations on the order of $\pm 50^\circ\text{C}$. MO-CVD allows in situ formation and growth of the semiconductor compound directly on the heated substrate where no etching specie is needed and accurate temperature controls are not necessary, thus making thin film growth a far less complicated matter.

Semiconductor Laser Construction

To excite a laser medium a population inversion must exist. In the junction laser application, necessary conditions for a population inversion are: 1) a large concentration of electrons in the conduction band and holes in the valence band, and 2) when population densities are high enough in the junction region.¹

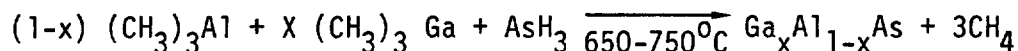
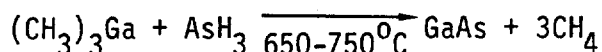
To construct a p-n junction laser, a junction of highly doped direct semiconductor material must be formed. In forming the junction, crystalline properties must be considered so that there is a relatively abrupt step and no excess stress to cause premature breakage. MO-CVD will produce repeatable heavily doped p type degenerate layers with Zinc as the dopant source and n type degenerate layers with Selenium as the dopant source. The layers need also be grown at various accurately controlled thicknesses.

Another important requirement is that of the resonant optical cavity which must be constructed of the correct geometrical orientation to the junction. The resonant cavity serves as an amplifying region and can be formed by careful polishing of the faces or cleaving along a perpendicular crystal plane.

For junction lasers to be operative at room temperature and commercially practical, the structures must be of efficient design and have good heat sinking. The most effective approach of providing good heat sinking is to lower the threshold (turn-on) current through the use of a heterostructure design. The object of a multilayered structure is to confine injected carriers to a narrow region and therefore the population inversion may build up at low current levels. Low current levels then translate into lower device temperatures and longer device lifetimes. The lasing action occurs at the p-n junction, although electron statistics dictate that some injected holes and electrons will stray from the junction and raise device temperature. In the heterostructure of Figure 1a an extra p type layer of GaAlAs is grown to form a potential barrier to confine electrons near the junction. In Figure 1b it can be seen that an extra p layer and n layer in the four layer structures are grown as potential barriers to confine both electrons and holes.² The confinement process works well to lower threshold currents and device heating although the growth of heterostructures by MO-CVD has been difficult at best to date.

Chemical Stoichiometry

MO-CVD implements two chemical reactions to fabricate GaAs and GaAlAs films.



Henceforth, the following shorthand notation shall be used:

$(\text{CH}_3)_3\text{Ga}$ - TMG (Trimethylgallium)
 $(\text{CH}_3)_3\text{Al}$ - TMA (Trimethylaluminum)
 AsH_3 - Arsine

The source of dopants to be used will be DEZ (Diethylzinc) for p type doping and H_2Se (hydrogen selenide) for n type doping. Thus films of GaAs and $\text{Ga}_x\text{Al}_{1-x}\text{As}$ composition are producible with either p or n type doping.

The silicon carbide pedestal in the reactor will be heated to 600°C then excess Arsine is forced into the system. When the reactor reaches the final specified reaction temperature (in the range $650\text{--}750^\circ\text{C}$) the flow of TMG and/or TMA is initiated. As necessary the proper dopant - DEZ or H_2Se - will be introduced at this time. The vapor phase metal organic and hydride materials will be forced to flow across the face of the substrate and will in this region at the proper temperature react to grow single crystal thin films on the GaAs substrate.

An important subtlety in the design philosophy involves the use of excess Arsine to react with the extra carbon atoms originating in the Methyl (CH_3) from TMG or TMA. Tying up the carbon atoms will disallow formation of carbonaceous residues which is an intolerable system impurity. The excess carbonaceous CH_4 and highly toxic Arsine along with the hydrogen carrier gas are all flushed to a ventilation hood as a safety precaution after passing through the reaction region.

Reactor Region

The reaction chamber shown in Figure 2 is a vertical quartz tube with a vertical mount for the silicon carbide pedestal which supports the GaAs substrate. Thin films of a homogeneous, single crystal nature will be grown on the substrate. The RF heater will heat the pedestal substrate and immediate reaction area to high temperatures. With vertical displacement from the reaction region the temperature will fall off exponentially. The temperature drop is due to glass being a poor heat conductor and a poor

absorber of electromagnetic energy. The temperature gradient is desired to prevent the metal-organics and hydrides from reacting until they arrive at the substrate surface. In this way, they can be deposited and grow along naturally oriented crystalline axes.

Before each deposition the reactor tube is purged with hydrogen under pressure flushing contaminants to the ventilation hood. The reactor is then pumped down just below atmospheric pressure before the temperature buildup begins. This helps to create a negative pressure differential such that reactants will flow across the substrate then be pulled through to the vent hood. It is critical that gas flow reactants be of uniform distribution while flowing across the substrate such that homogeneous smooth films will result.

Metal-Organic Material Handling

It is important to control accurately film thickness and composition. When reviewing the chemical stoichiometry it is seen that the amount of GaAs or GaAlAs produced will be a function of the quantity of TMG and/or TMA involved in the reaction. Both TMG and TMA are extremely volatile liquids and thus require special consideration. The final system design (Figure 3) requires that both metal organic liquids be kept in stainless steel dewars at 0°C, then by bubbling a metered amount of H₂ through the liquid some of the liquid will be forced into its vapor phase and swept into the reactor region. By this design the concentration of TMG and TMA involved in the reaction will be directly controlled by the flow rate of the H₂ bubbling gas and the temperature of the dewar. DEZ - the p-type dopant source - will be kept at 0°C in a dewar and handled similar to the TMG while hydrogen selenide - the n-type dopant - can be introduced simultaneously with the TMG or TMA but requires no special handling.³ Dopant concentrations in the film will be controlled by flowmeter settings.

All flow lines, valves, and meters will be made of #316 stainless steel which will allow minimal residue buildup or premature reactions previous to the reactor region. Impurities will destroy film quality and must be eliminated so that single crystal films of high purity may be produced.

Gas Controls

One of the most attractive qualities of the MO-CVD system is that the entire chemical process is controllable by a simple set of flowmeter dial adjustments (Figure 3). Since human engineering is a valuable part of any mechanical system, complete control by simple mechanical adjustments is extremely valuable in all commercial applications of the system.

MO-CVD will lend itself with relative ease to computer system control. For example, any of a number of commercially available mini-computers could handle monitoring flow rates and electronically open and close valves according to various timing sequences. To have complete system control the processor would also have to be able to purge and evacuate the reactor upon command. These easily automated functions would be the only ones needed to achieve film growth.

Analysis

The end product of the data analysis will be a standards manual describing a simple procedure for growing GaAs and GaAlAs of various doping levels. Of most critical concern will be film composition and thickness, as the description of electrical parameters is beyond the scope of this paper.

On the subject of film composition GaAs and $\text{Ga}_x\text{Al}_{1-x}\text{As}$ are expected where $\text{Ga}_x\text{Al}_{1-x}\text{As}$ implies films spanning the range from $\text{Ga}_{.1}\text{Al}_{.9}\text{As}$ through $\text{Ga}_{.9}\text{Al}_{.1}\text{As}$. Experimental determination of film composition will be handled accurately by Auger spectroscopy which is based on the principle that as electrons of various energies are incident on the film surface different elements either absorb or scatter the electrons in such a way that they can be identified. By scanning a section of the film surface - which should be homogeneous - relative concentrations can be defined with good accuracy. By fabricating numerous experimental films with different relative concentrations of chemical reactants and measuring film compositions a standards table will be produced relating flowmeter settings and film composition.

With regards to film thickness, an interesting problem develops in that the films will be transparent. Two devices will be used for measuring thickness depending on the optical properties of the film - the angstrometer

and ellipsometer. Basically film thickness will be determined by a measure of how light waves bend while propagating through the transparent film. Film thickness will be a function of the length of time vapor phase reactants flow across the substrate surface with anticipated rates of 500-1000 Angstroms per minute. Therefore, if the temperatures of the metal-organic liquids are kept constant, film thickness can be tabulated as a function of time.

Finally the scanning electron microscope (SEM) will be used to investigate surface characteristics. The SEM will determine for film smoothness, surface homogeneity and single crystalline properties.

Applications

In a study released recently by Frost and Sullivan of New York entitled "US Laser Technology and Markets in Commerce and Industry" significant growth is projected in virtually every laser market. The semiconductor laser market is expected to realize the largest growth rate of 35% rising from a current level of \$5.5 million to a projected \$20 million in 1983 and \$60 million in 1986. Another impressive statistic is reflected in the anticipated growth of optical communication markets from the current \$27 million to \$180 million in 1983.⁴ Although there are still technological problems to overcome, much of the anticipated growth stems directly from improvements in semiconductor laser device quality and fabrication technique.

MO-CVD is among the technological improvements that can make semiconductor lasers economically feasible while simultaneously producing high quality devices.

Conclusion

The decomposition of TMG or TMA in the presence of excess Arsine should produce crystal growth of III-V compounds on a GaAs substrate. Doping concentrations of excess holes and electrons are accomplished by introducing DEZ and H₂Se respectively. The MO-CVD process is designed in a manner such that the control of film composition, thickness, and doping is a matter of flowmeter adjustments, temperature control of reactants, and reaction time

control. MO-CVD negates the use of multi-temperature zones and makes semiconductor film growth compatible with that of elemental semiconductors thus allowing MO-CVD produced films to be studied by techniques exactly similar to those used on elemental semiconductor electro-optic materials.

Acknowledgements

The author would like to thank H. M. Manasevit and W. I. Simpson for original research; Dr. A. B. Buckman for thesis direction; Dr. J. Roessett for organizational sponsorship; and J. Jackson organization president.

References

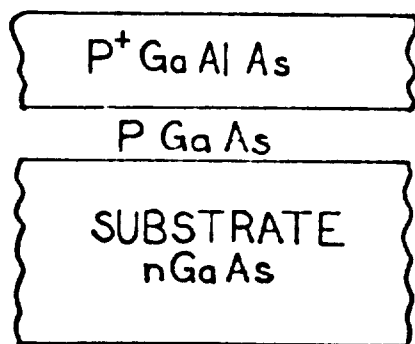
1. Amnon Yariv, Introduction to Optical Electronics, New York: Holt, Rienhart and Winston, 1971, Ch 7.8 "Semiconductor Lasers", pp 176-182.
2. Ben Streetman, Solid State Electronic Devices, Prentice-Hall, Inc. Englewood Cliffs, N.J. 1972, Ch. 7 "Lasers", pp 262-271.
3. H. M. Manasevit and W. I. Simpson, J. Electrochemical Society Vol 116, No. 12, p 1725 (1969)
4. Electro Optic System Design, February 1980, p 8

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately-owned rights.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

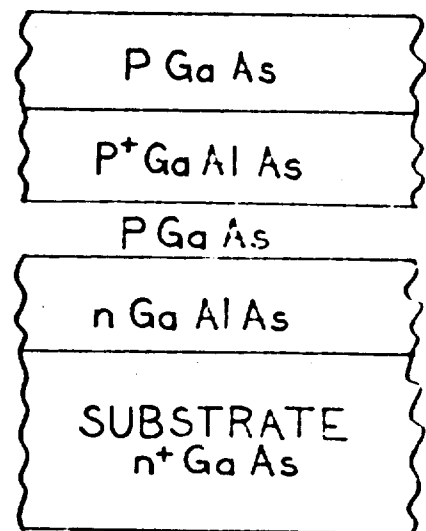
SEMICONDUCTOR LASERS



2 LAYER HETEROJUNCTION
ON $GaAs$ SUBSTRATE

Figure 1a

LASING REGION



4 LAYER HETEROSTRUCTURE
ON $GaAs$ SUBSTRATE

Figure 1b

MO-CVD REACTOR REGION

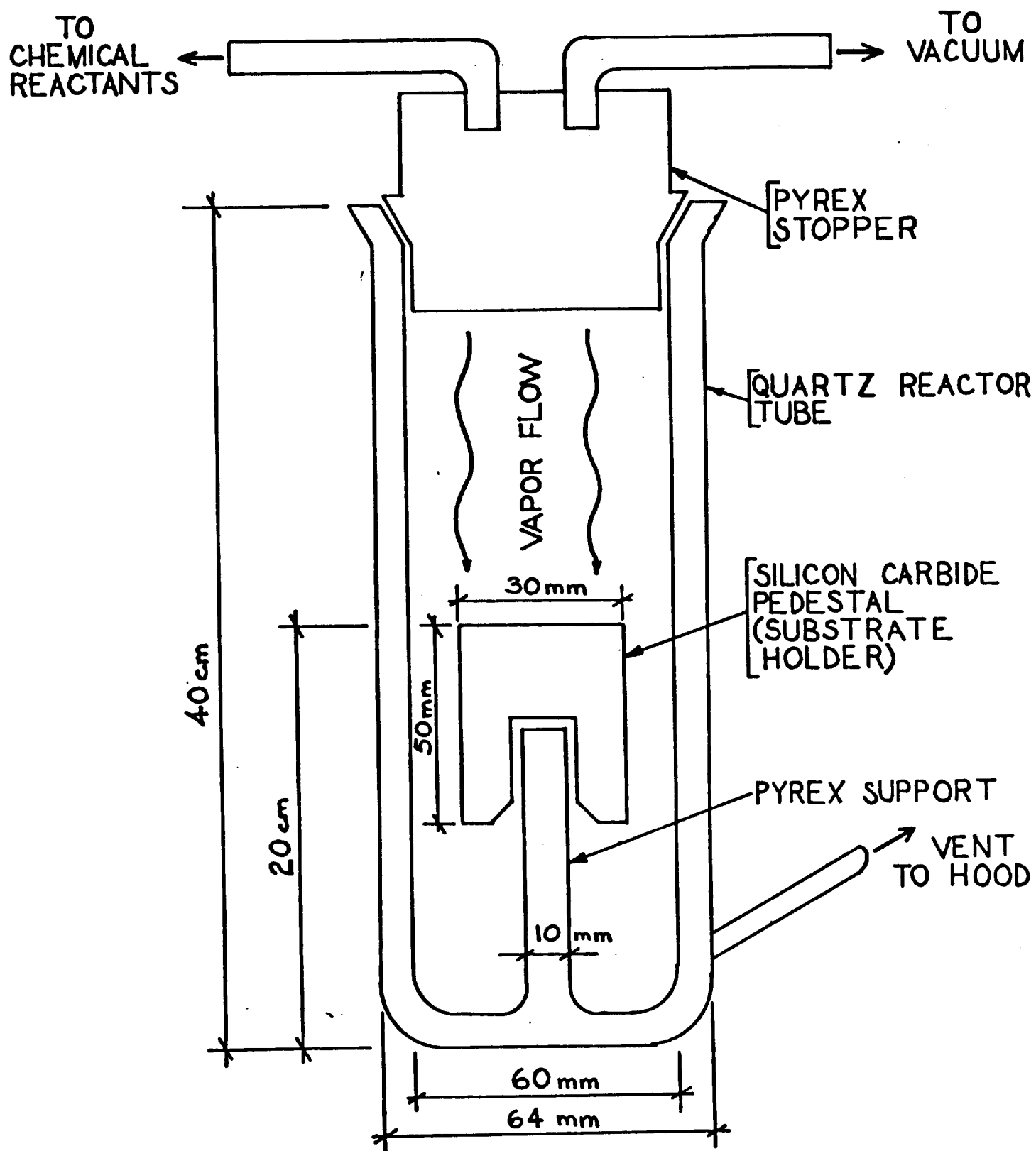
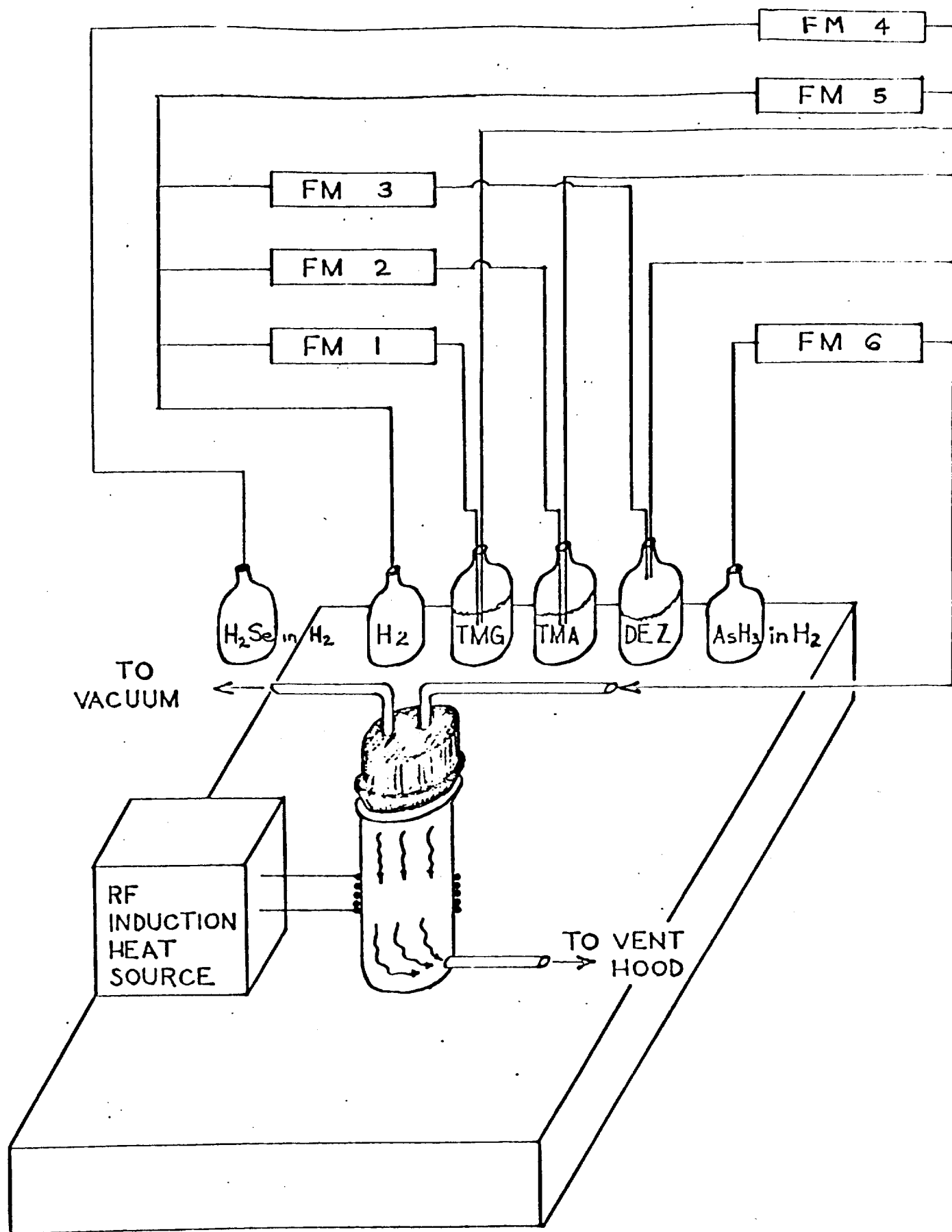


Figure 2



FM—FLOWMETER

Figure 3

